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14. ABSTRACT This report summarizes the development of a new class of electroactive polymer, high energy electron irradiated P(VDF-TrFE) copolymer, which exhibits a ultrahigh electrostrictive strain with high elastic energy density and high electromechanical coupling factor. The processing conditions on the electromechanical performance of the irradiated copolymer were systematically investigated. The electromechanical responses were characterized as a function of temperature, mechanical load, and frequency. The results demonstrate that the newly developed electrostrictive copolymer has a high load capability (up to 45 MPa) and can maintain the high strain level to high frequency (~ 100 kHz) which are suitable for Navy underwater acoustics applications. In addition, the irradiated copolymer also possesses a high room temperature dielectric constant, the highest among the known polymers, and shows many features resembling the relaxor ferroelectric system, which makes it the first known relaxor ferroelectric polymer. The changes in the structure, morphology, and transitional behavior were also characterized in terms of WAXS, DSC, FT-IR, and crosslinking density measurement.					
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21 Jun 2000
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Electroactive Polymers for Smart Skin Applications

(June 1, 1997 to June 30, 2000)

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1. Introduction :

Advances in transducer and actuator technology are constantly demanding the development of new materials, which can generate a large electric field induced strain with high precision and speed, and having a low fatigue rate for a long lifetime and high reliability for the development of robots, artificial muscle, active control and smart systems. Although several types of actuator technologies have been demonstrated or proposed based on the electromagnetic, piezoelectric and electrostrictive effects. But each technology exhibits limitations in one or more performance parameters such as strain, elastic energy density, speed of response and efficiency. Therefore, there is a strong demand of a general purpose electroactive material with overall improvement in performance as an transducer, actuator and sensor.

Under this program we found a P(VDF-TrFE) copolymer system under a proper electron irradiation treatment, can exhibit massive electrostrictive strain with high elastic energy density. Although, several electroactive polymers such as polyurethane, polybutadiene, silicone rubber etc, were observed to generate very high electric field induced strain up to 6-11% due to Maxwell stress effect. But due to their low elastic modules (0.7 ~17MPa), the driving force reduces significantly with the increase in mechanical load. Therefore, in order to analyze the performance of irradiated copolymer system for different actuator and transducer applications, we characterized the irradiated copolymer response under different static mechanical loads and frequency.

Interestingly, it was found that by modifying the morphology and choosing the proper irradiation conditions the electromechanical properties can be tuned. For example, for stretched films the electric field induced strain and electromechanical coupling coefficient are higher along the stretching direction in comparison to the thickness or applied electric field direction, whereas for unstretched films the strain and piezoelectric coefficient along the field is always higher than the perpendicular directions.

In addition, being a polymeric material, the acoustic impedance level match well with the human tissue and there is no mechanical fatigue at high strain level. In conclusion, the invented electrostrictive polymer with the improved electrical properties offers a great improvement in characteristics required for capacitor, actuator, and transducer industry.

2. Charaterization of Electrostrictive and Electromechanical Properties :

2.a Giant Electrostrictive Strain :

The electric field induced strain was found to be improved remarkably after irradiation. As shown in figures 1(a) and 1(b), the maximum longitudinal strain level, i.e. strain along the thickness direction, -4 and -5 % were observed under around 150 MV/m for PVDF-TrFE, 50/50 and 68/32 mol % unstretched films, irradiated with 40 Mrad at 120 °C using 2.55 MeV electrons and 60 Mrad at 100 °C using 1.0 MeV electrons, respectively.

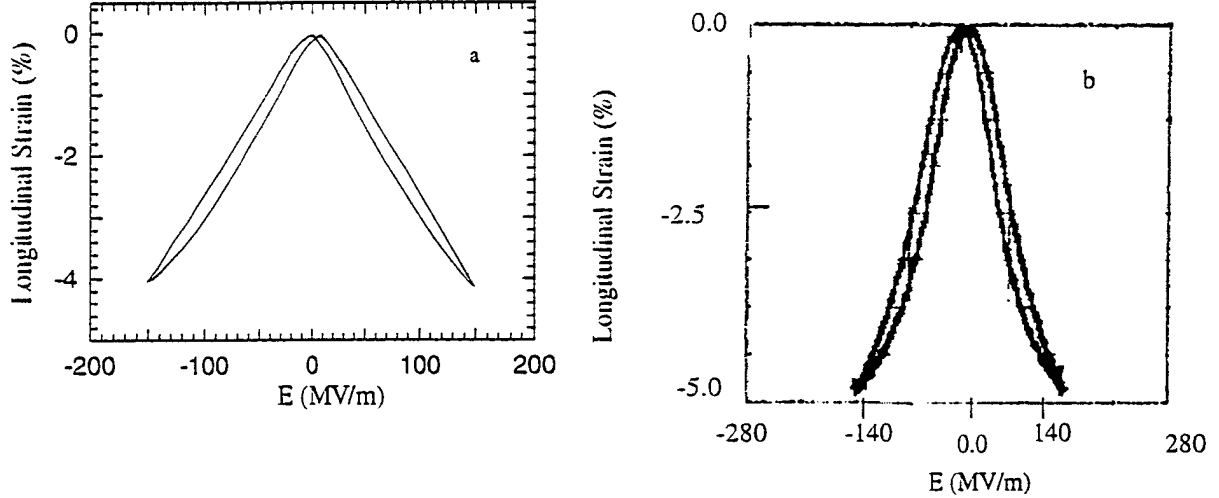


Figure 1: The electric field dependence of longitudinal strain of P(VDF-TrFE) copolymer (a) 50/50 mol% unstretched film irradiated with 40 Mrad, 2.55 MeV at 120 °C and (b) 68/32 mol % unstretched film irradiated with 60 Mrad, 1.0 MeV electrons at 100 °C.

The induced strain exhibits very low hysteresis and followed the electrostrictive relation, $S = QP^2$ between strain (S) and polarization (P); here Q is an electrostrictive coefficient. The

electrostrictive strain was reproducible under a cyclic electric field. This attribute is an attractive feature for many transducer and actuator applications, for example, for the actuators used in astronomy and optical communication for controlling optical path lengths of the order of optical wavelengths.

Table-I : Comparison of Strain and Strain Energy Densities.

Materials		Y (GPa)	S_m (%)	$YS_m^2/2$ (J/cm ³)	$YS_m^2/2\rho$ (J/kg)
Electrostrictive	S_3	0.50	5.0	0.6	300
PVDF-TrFE	S_1	1.3	3.5	0.8	400
Piezoceramics		64	0.2	0.13	17
Magnetostrictor		100	0.2	0.2	21.6
PZN-PT Single Crystal		7.7	1.7	1.0	131
Polyurethane		0.017	11	0.1	83

However, many soft polymers can also generate a very high strain level due to an electrostatic effect. Therefore, in addition to the strain level, other parameters such as the volumetric energy density ($YS_m^2/2$) related with device volume and gravimetric energy density ($YS_m^2/2\rho$) related with device weight were calculated in order to evaluate the actuator material performance. Here ρ is the density, Y is Young's modulus, and S_m is the electric field induced strain in the copolymer films. Table-I compares the newly discovered copolymer with several currently known materials including the ferroelectric relaxor single crystal PZN-PT, which was discovered recently to possess an ultrahigh strain response. As we can see, the electrostrictive P(VDF-TrFE) copolymer exhibits higher elastic energy densities comparable with the current piezoceramics.

2.a.i Effect of Copolymer Composition, Processing and Electron Irradiation Conditions:

One of outstanding characteristic of irradiated copolymer system is that by choosing the proper copolymer composition, by modifying the polymer morphology (stretched vs. unstretched) and by controlling the irradiation parameters (irradiation energy, temperature and dose), the magnitude of the electromechanical properties can be tuned.

Effect of Copolymer Composition:

As shown in figure 2, the maximum induced strain level observed for each composition under different irradiation conditions increases in the following order, 50/50 < 65/35 < 68/32 mol%. However, if we compare the strain hysteresis loop, the hysteresis loop decreases in the following order 68/32 > 65/35 > 50/50 mol%.

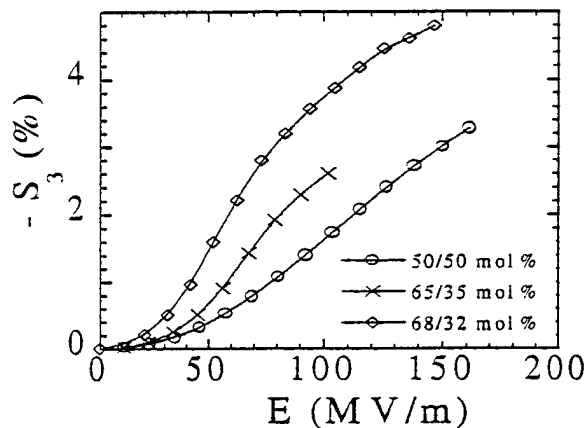


Figure 2 : Effect of P(VDF-TrFE) copolymer molar composition on the induced longitudinal strain (S_3) level.

These results were obtained from 50/50 mol% copolymer films irradiated with 2.55 MeV electrons, at 23 °C for 100 Mrad dose, 65/35 mol% copolymer films irradiated with 2.55 MeV electrons, at 95 °C for 60 Mrad dose, and 68/32 mol% copolymer films irradiated with 1.00 MeV electrons, at 100 °C for 70 Mrad dose.

Effect of Stretching:

Along with the selecting the proper composition, the magnitude and hysteresis of induced strain in different directions, as shown in figure 3(a) can be tailored by modifying the copolymer morphology. For example, in unstretched films the S_3 / S_1 ratio is about -4 , while for stretched films the same ratio is -0.97 (figure 3(b)). However, the strain measured perpendicular to the stretching and applied field direction (S_2) is always smaller than the strain measured along the field direction (longitudinal strain, S_3) and the strain measured along the stretching direction (transverse strain, S_1).

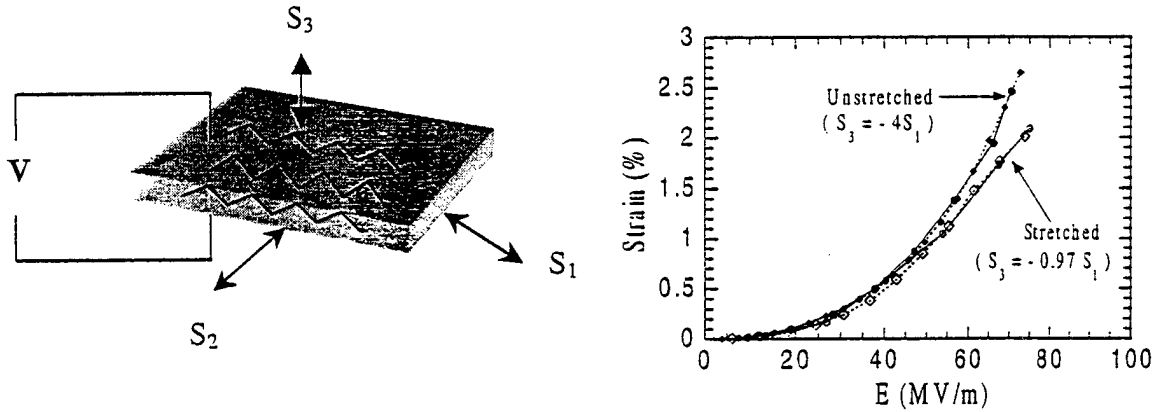


Figure 3: (a) Schematic induced strain level measured in different directions, (b) The comparison of the electric field induced longitudinal (S_3 , solid lines) and transverse (S_1 , dashed lines) strains for P(VDF-TrFE) 65/35 mol% unstretched films irradiated with 60 Mrad dose at 120°C and stretched films irradiated with 60 Mrad dose at 95°C.

Effect of Electron Irradiation Conditions:

The electron irradiation conditions were found to be effected greatly by the electromechanical properties of this newly developed electrostrictive copolymer system. Therefore, after selecting the proper composition and modifying the morphology, the copolymer films were irradiated

under different irradiations conditions in order to find out the optimum electromechanical properties as demonstrated in figures 4(a), 4(b), and 5.

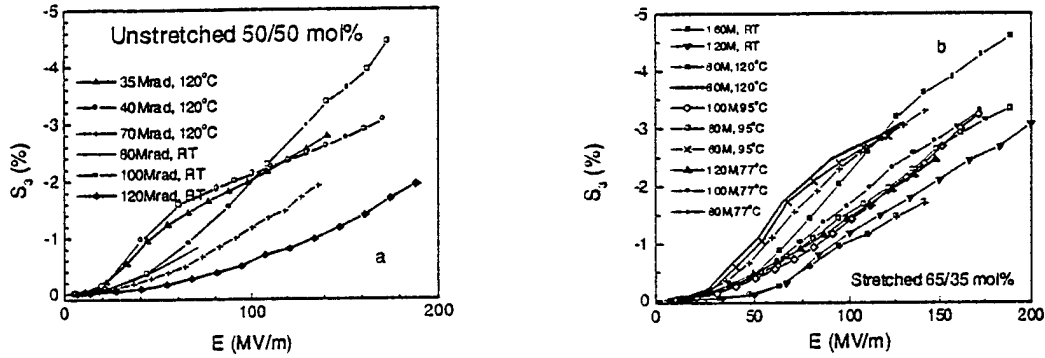


Figure 4: Longitudinal strain (S_3) measured for (a) 50/50 unstretched and (b) 65/35 mol% stretched P(VDF-TrFE) copolymer films irradiated with 2.55 MeV electrons with different irradiation dose and temperature as indicated in figure.

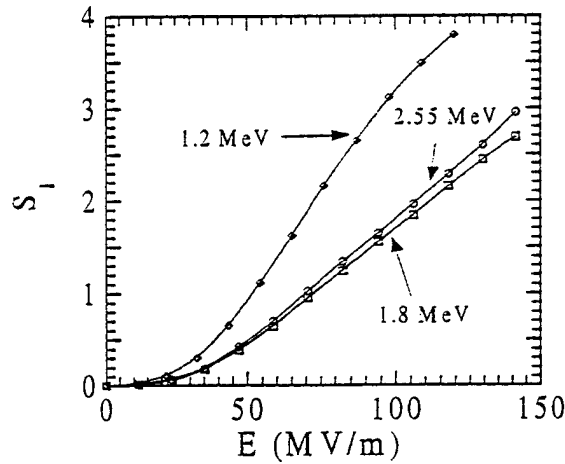


Figure 5: Effect of electron energy on Transverse strain (S_1) measured for stretched 68/32 mol % copolymer films, irradiated at 100°C with 70 Mrad dose.

2.a.j Effect of External Mechanical Load on the Electrostrictive Strain:

The 65/35 mol % stretched films irradiated at 95°C with 60 Mrad dose using 2.55 MeV electrons were used to measure the transverse strain under different tensile stresses along the stretching direction. As can be seen from figure 6(a), under a constant electric field, the transverse

strain initially increases with the load and reaches a maximum at the tensile stress of about 20 MPa. Upon further increase of the load, the field induced strain is reduced. One important result revealed by the data is that even under a tensile stress of 45 MPa, the strain generated is still nearly the same as that without load, indicating that the material has a very high load capability.

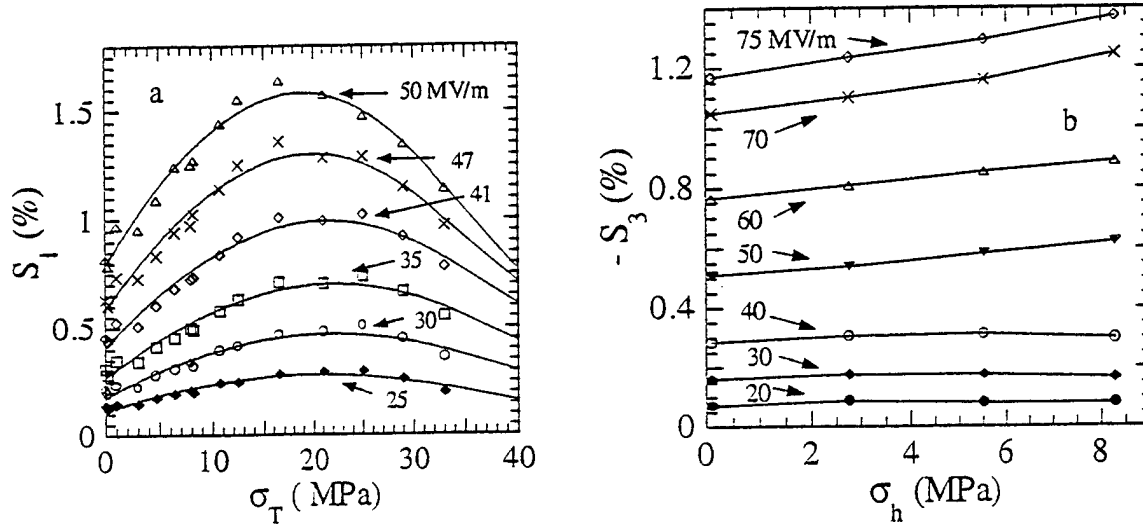


Figure 6 : (a) Effect of tensile stress (σ_T) on electric field induced transverse strain (S_1) measured at room temperature under different driving electric field strengths measured for 65/35 mol% copolymer stretched film irradiated with 2.55 MeV electrons at 95 °C with 60 Mrad dose (b) effect of hydrostatic pressure (σ_h) on electric field induced longitudinal strain (S_3) measured at room temperature under different driving electric field strengths measured for unstretched 65/35 mol% copolymer film irradiated with 2.55 MeV electrons at 95 °C with 60 Mrad dose.

The longitudinal strain for unstretched 65/35 mol% films irradiated with 2.55 MeV electrons at 95 °C with 60 Mrad dose as a function of hydrostatic pressure is presented in figure 6(b). As can be seen, at a low driving electric field, the strain does not change much with pressure. On the other hand, for high fields it shows increases with pressure. Due to a limitation of the experimental set-up, we could not apply a pressure higher than 8.2 MPa. The results from both experiments clearly demonstrate that the electrostrictive P(VDF-TrFE) copolymer has a

high load capability and maintains its strain level even under a very high load, which is in contrast to many other electrostrictive polymeric materials.

2.a.k Effect of Temperature and Frequency on the Electrostrictive Strain :

Effect of Temperature:

Figures 7(a) and 7(b) show the change in the longitudinal strain versus temperature measured for 65/35 mol % copolymer films irradiated with 2.55 MeV electrons at 95°C with 60 Mrad dose and 68/32 mol % copolymer films irradiated with 1.00 MeV electrons at 100 °C with 70 Mrad dose, respectively. As can be seen, for both type of copolymer compositions, the induced strain is almost constant up to 80 °C.

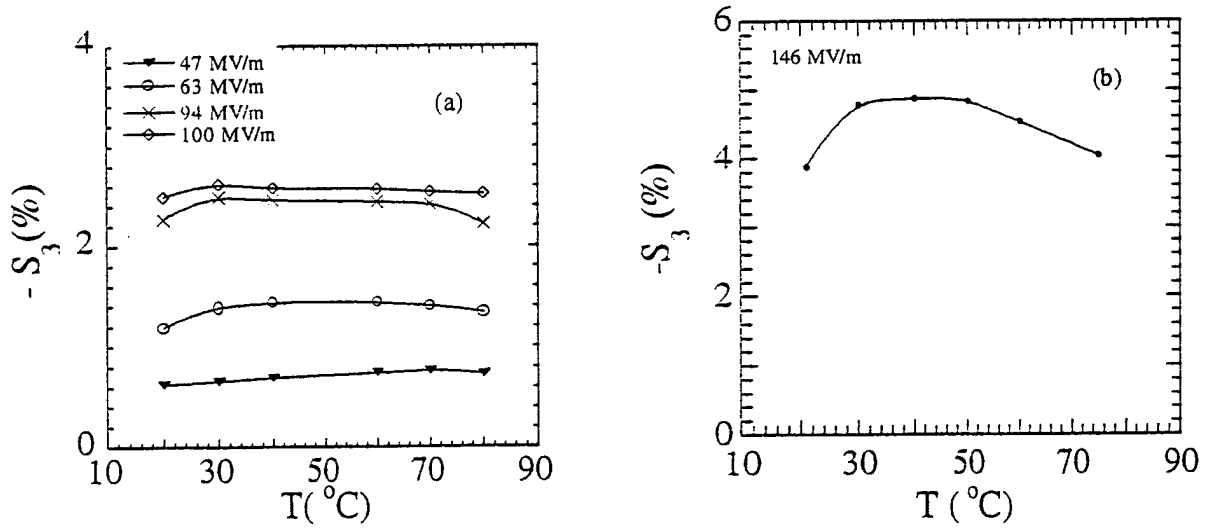


Figure 7: Variation in electric field induced transverse strain (S_1) as a function of temperature measured under stress free conditions for (a) 65/35 mol % copolymer films irradiated with 2.55 MeV electrons at 95 °C with 60 Mrad dose at different electric field strengths as marked in figure, and (b) 68/32 mol % copolymer films irradiated with 1.0 MeV electrons at 100 °C with 70 Mrad dose.

Effect of Driving Frequency:

The laser interferometer set-up was used to measure the strain at higher frequencies up to 5 kHz under 20 MV/m field. However, in this set-up we could not apply the high electric field. Therefore, the change in the induced strain at higher frequencies with respect to the strain at 1 Hz frequency is presented in figure 8. The electric field induced strain in electrostrictive copolymer films is found to be reduced almost 50% at 5 kHz frequency in comparison to the strain at 1Hz. Interestingly, if we increase the temperature slightly for example 42°C, the reduction in strain at 5 kHz is only 15%. Also the change in the strain with the frequency does depend on the induced strain amplitude as we can see that change in the ratio of the strain measured from laser interferometer set-up induced by 20 MV/m driving field is almost the same as measured from bimorph based set-up up to 70 Hz induced by 100 MV/m driving field. These features are unique for polymeric materials and clearly demonstrate the ability to maintain the electrostrictive strain over a broad frequency and temperature range.

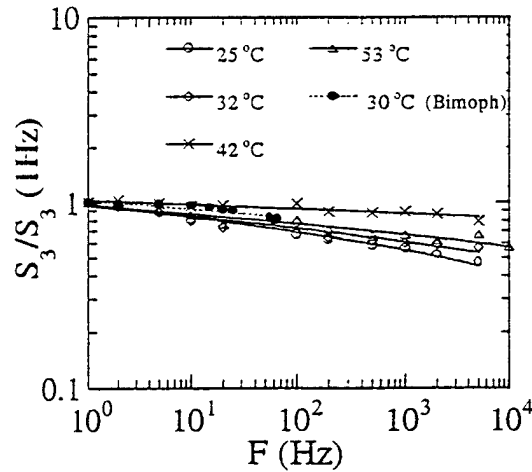


Figure 8. The ratio of longitudinal strain (S_3) at higher frequencies with respect to the strain at 1 Hz (open circles) as a function of frequency measured using laser interferometer at (a) 25°C, and (b) 33°C temperature; for unstretched 68/32 mol % P(VDF-TrFE) copolymer films irradiated at 105°C with 1.0 MeV electrons for 70 Mrad dose. In figure 4 (b), the strain data (cross dots) measured using the bimorph based sensor is also presented.

2.a.1 Induced Strain under Unipolar and Bipolar Driving Fields :

The induced strain level was examined under both bipolar and unipolar driving electric fields to compare the performance under these conditions. For electrostrictive materials, although in some actuator applications it can be driven with bipolar field, in most cases the driving field will be unipolar. Hence, it is very important for the material to have nearly the same performance under these two different driving conditions.

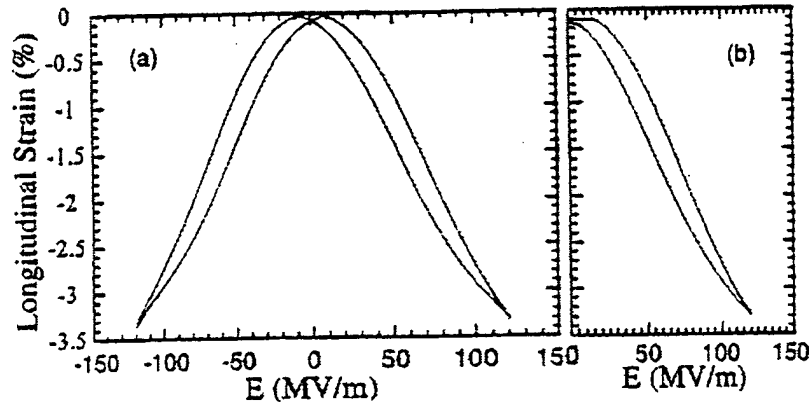


Figure 9 : The field induced strain at room temperature: (a) under bipolar driving field, (b) under unipolar driving field measure for unstretched 65/35 mol % P(VDF-TrFE) copolymer films irradiated at 120 °C with 2.55 MeV electrons for 60 Mrad dose.

As presented in figure 9, the strain was measured at room temperature under both driving fields using the 65/35 mol% copolymer films irradiated at 120°C with 60 Mrad dose with 2.55 MeV electrons. It can be seen clearly that copolymer exhibits nearly the same strain level under both type of driving fields. Slightly lower value in unipolar strain (3%) in comparison to bipolar strain (3.3%) is due to the existence of small hysteresis. The irradiated copolymer nearly recovers its original zero field state after the applied field is reduced to zero. This information are very important to select the material as an actuator and clearly demonstrates that induced strain level in irradiated copolymer is reproducible under the cyclic electric field and the same for both unipolar and bipolar driving electric fields.

2b Improved Piezoelectric and Electromechanical Properties:

Piezoelectric Properties :

Although after irradiation, copolymer behaves as an electrostrictive material, a high piezoelectric state can be induced by applying a dc bias electric field as shown in

figure 10. The maximum piezoelectric

coefficient, $d_{31} = 300 \text{ pm/V}$ and $d_{33} = -383 \text{ pm/V}$

was observed under 40 MV/m and 75 MV/m bias

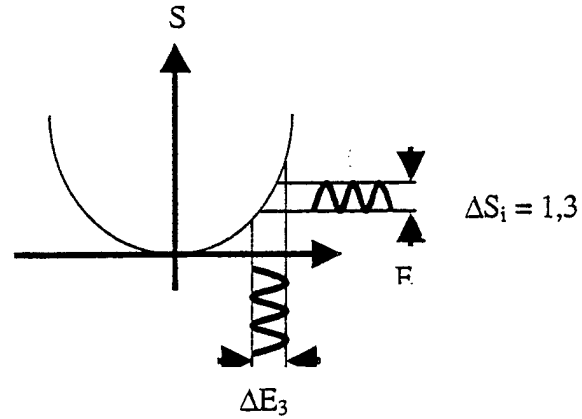


Figure 10

field for irradiated stretched 68/32 mol% copolymer films, irradiated with 70 Mrad dose at 100 °C using 1.2 MeV electrons and unstretched 68/32 mol% copolymer films, irradiated with 70 Mrad dose at 100 °C using 1.0 MeV electrons, respectively (figures 11(a) and 11(b)). These values are almost ten times higher than the maximum values observed for normal poled ferroelectric copolymer systems and are comparable to the piezoelectric coefficient of conventional piezo-ceramic materials for example PZT-5H ($d_{33} \sim 593 \text{ pm/V}$).

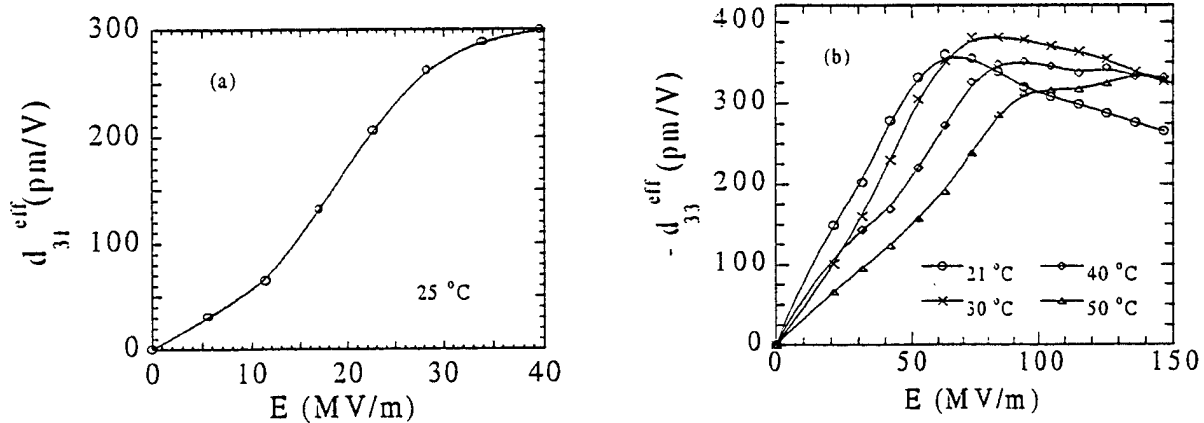


Figure 11 : Effective piezoelectric coefficients; (a) d_{31}^{eff} measured for stretched P(VDF-TrFE) copolymer films irradiated at 100°C with 70 Mrad using the 1.2 MeV electrons, and (b) d_{33}^{eff} measured for unstretched P(VDF-TrFE) copolymer films irradiated at 100°C with 70 Mrad using the 1.0 MeV electrons.

Electromechanical Properties:

The quasi-static electromechanical coupling factor for electrostrictive materials has been derived by Hom et al., where the coupling factor depends on the induced polarization level P_B and strain S_i under a given electrical field, i.e.,

$$k_{3i}^2 = \frac{kS_i^2}{s_{ii}^P \left[P_B \ln \left(\frac{P_S + P_B}{P_S - P_B} \right) + P_S \ln \left(1 - \left(\frac{P_B}{P_S} \right)^2 \right) \right]} \quad (1)$$

where $i=1$ or 3 , corresponding to the transverse or longitudinal direction (for example, k_{31} , is the transverse coupling factor) and s_{ii}^P is the elastic compliance under constant polarization. Using the polarization and elastic modulus data, the quasi-static transverse coupling factor k_{31} is calculated and presented in figure 12(a). As can be seen, at near room temperature k_{31} can be more than 0.45, which is by far the highest coupling factor reported in ferroelectric polymers and even higher than k_{31} from most of the piezoceramics. Since in many applications such as micro-electro-mechanical-systems (MEMS), electrical power generation from ocean waves and artificial muscles, it is the transverse strain that is often used; therefore, a high transverse coupling factor is highly desirable.

Also by using eq.(1) with the elastic modulus and polarization data for unstretched 68/32 mol% copolymer films irradiated with 1.0 MeV electrons at 105°C for 70 Mrad dose, the longitudinal coupling factor (k_{33}) is determined and presented in figure 12(b). At near room temperature and under 80 MV/m electric field, the value of k_{33} more than 0.3 can be achieved. Assuming the elastic compliance does not change with electric field, the change in the electromechanical and piezoelectric properties with temperature is due to the change in induced polarization level.

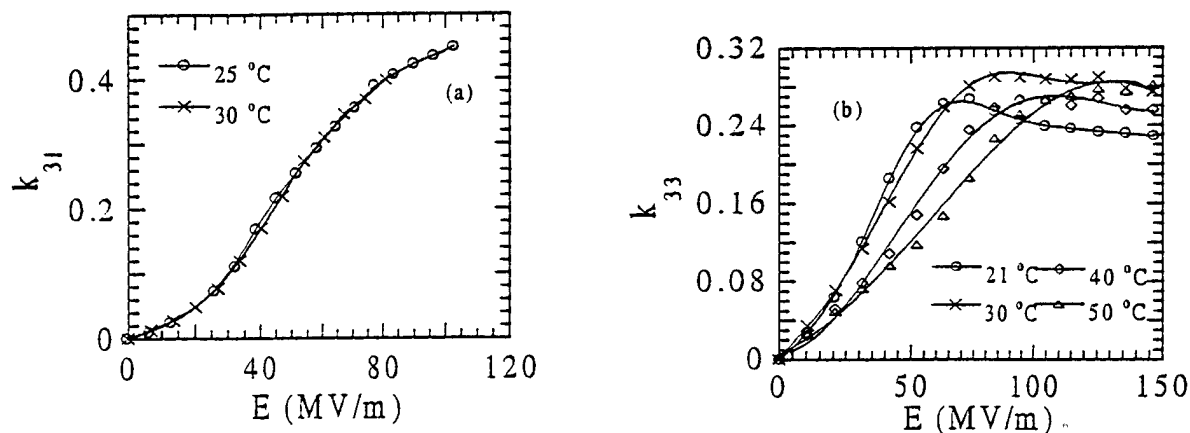


Figure 12: The change in the electromechanical coupling factor (a) k_{31} with applied electric field at different temperatures; measured for stretched 68/32 mol % P(VDF-TrFE) copolymer films irradiated at 100°C with 1.2 MeV electrons for 70 Mrad dose. (b) k_{33} with driving electric field and temperature; measured for unstretched 68/32 mol % P(VDF-TrFE) copolymer films irradiated at 105°C with 1.0 MeV electrons for 70 Mrad dose.

2.c Improved Dielectric Properties:

Figures 13(a) and 13(b) show the irradiation effect on the dielectric constant for unstretched 50/50 mol% and stretched 65/35 mol% copolymer films irradiated at 120 and 95°C using 2.55 MeV electrons, respectively. As can be seen that after the irradiation, the dielectric peak shifts towards lower temperature in comparison to the unirradiated film, and therefore, increases the dielectric constant remarkably at room temperature.

Similar to the strain, the dielectric constant can also be tailored using different material processing and irradiation conditions, for example, with increasing irradiation dose the dielectric peak can be made broader and broader. On the other hand, as can be seen by comparing the dielectric constant for stretched and unstretched PVDF-TrFE (65/35 mol%) film irradiated at 95°C with 60 Mrad dose using 2.55 MeV electrons (figure 13), by stretching the film not only the dielectric constant value can be improved, but also, the thermal hysteresis

associated with the dielectric constant can be reduced significantly. The dielectric constant is around 67 and a loss less than 2% was observed at 1 kHz near room temperature in 65/35 mol% stretched films irradiated at 95°C with 40 Mrad dose using 2.55 MeV electrons (figure 13(b)). To our knowledge, the electrostrictive PVDF-TrFE copolymer shows the highest dielectric constant with low dielectric loss at room temperature among the known polymer dielectric materials.

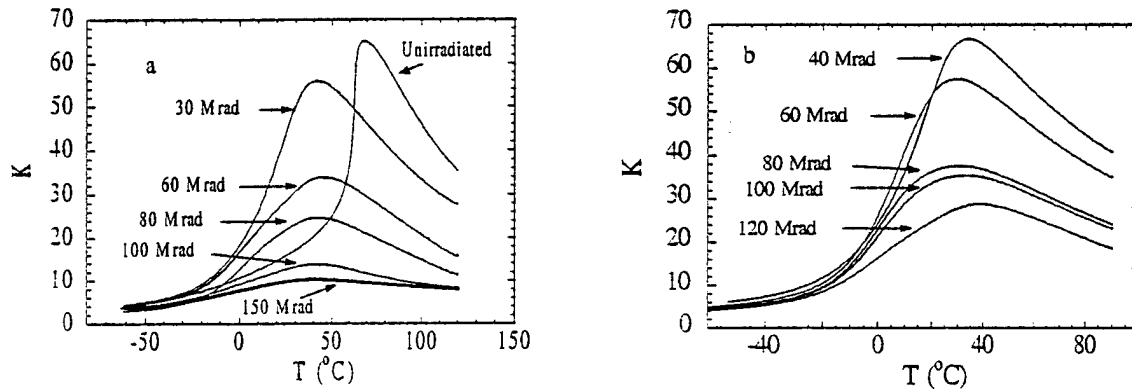


Figure 13: The dielectric constant (K) measured at 1 kHz as a function of temperature for P(VDF-TrFE) (a) 50/50 mol% unstretched films irradiated with 2.55 MeV electrons at 120°C, (b) 65/35 mol % stretched films irradiated with 2.55 MeV electrons at 95°C for different doses as indicated.

Relaxor Behavior:

Another interesting feature observed during this study is that the irradiated copolymer films show relaxor ferroelectric behavior, a class of material under extensive investigation due to many peculiar features and potential for broad range applications. In comparison to normal ferroelectrics, relaxor ferroelectrics are characterized by the presence of diffuse and rounded maximum in the temperature dependence of the dielectric permittivity, which exhibits strong relaxation dispersion for a wide frequency range. It was found that the irradiated PVDF-TrFE copolymer system shows a broad dielectric peak, which shifts towards higher temperature with increasing frequency (figure 14(a)) and follow the Vogel-Fulcher law (as shown in inset of

figure 14(a)), an empirical law which is applicable for the system which undergoes relaxation freezing below certain temperature such as glassy and relaxor ferroelectric materials and can be expressed as :

$$f = f_0 \exp\left[\frac{-U}{k(T_m - T_f)}\right] \quad (2)$$

where T_m is the dielectric constant peak temperature, f is the frequency, and k is the Boltzman constant.

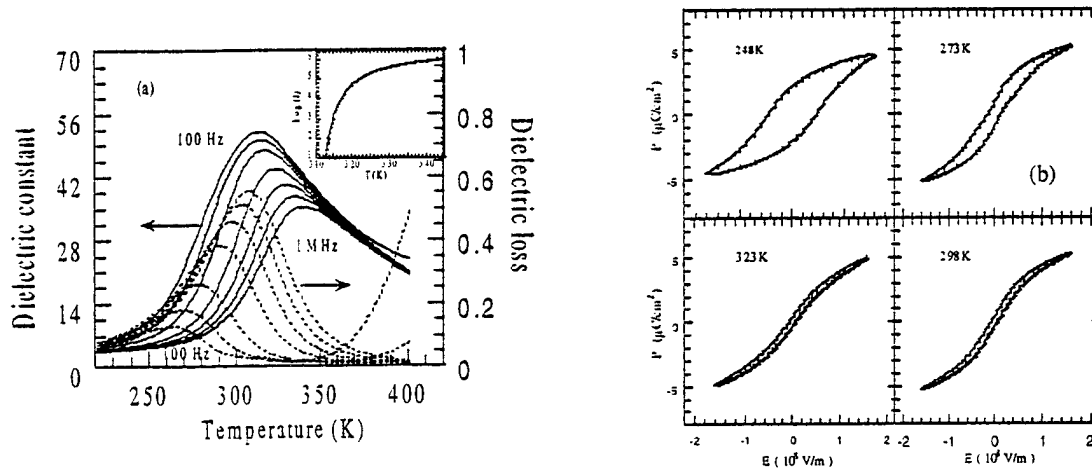


Figure 14: (a) Dielectric constant (solid lines) and dielectric loss (dashed lines) as a function of temperature and frequency. The inset shows the fitting of the Vogel-Fulcher law, where the solid line is the fit and the circles are the data points. (b) change in the polarization hysteresis loop with temperature measured for 50/50 mol% copolymer films, irradiated with 2.55 MeV electrons at 120 °C with 40 Mrad dose.

In addition, relaxors show a slim polarization hysteresis loop near dielectric maxima. But as temperature is reduced from dielectric maxima (T_{\max}) the hysteresis loop gradually broadens and finally transforms into a regular rectangular loop at a temperature well below T_{\max} .

The square to slim hysteresis loop is evident in figure 14(b). The polarization behavior becomes hysteretic at -25°C temperature with remanent polarization, $P_r = 2.1 \text{ mC}/\text{cm}^2$,

saturation polarization, $P_s = 40 \text{ mC/ cm}^2$ and critical field, $E_c = 45.5 \text{ MV/m}$. However, with increase in the temperature the polarization reduces gradually and shows a slightly non linear polarization loop near 50°C i.e. near T_{max} .

These results elucidate that material after irradiation behaves like relaxor ferroelectric material. The results obtained from X-ray scans, Raman spectra, DSC and crosslinking measurements show that electron irradiation breaks up the coherent polarization domains in the normal ferroelectric to nano scale polar region, introducing defects randomly by introducing gauche bonds in long trans planar polymer chain and crosslinking in the crystalline region.

3. Structural Characterization:

3.a X-ray Analysis:

Figures 15(a) and 15(b) show X-ray patterns obtained from unstretched and stretched 50/50 mol% films irradiated for different doses At 95°C using 2.55 MeV electrons, respectively. Consistent with the earlier studies, before irradiation, the unstretched films exhibit two peaks at $2\theta = 18.79^\circ$ (4.72 \AA) and 19.28° (4.59 \AA). The peak at 4.72 \AA is due to the hexagonal packing of 3/1-helical chains generated due to the presence of TG and TG' defects and second is due to similarly packed trans-planar chains. However, the stretched films show only one peak at 4.68 \AA spacing and therefore, show that the stretching not only transform the chain segments containing 3/1 helical conformation, but also pack more closely and more regularly the chain segments that already are in the trans-planar conformation.

After 40 Mrad of irradiation, only one peak is observed at a lower angle for both the unstretched and stretched films and thus, clearly indicates the expansion of the lattice due to the introduction of defects in the crystalline phase during the irradiation. Upon 60 Mrad irradiation, the peak appears at 4.84 \AA for both unstretched and stretched irradiated films. The corresponding lattice spacing is close to the paraelectric phase of the non-irradiated copolymer

films determined from X-ray above the Curie temperature and therefore indicates the conversion of ferroelectric phase of the copolymer to the paraelectric phase. The non-polar phase induced by irradiation is permanent and cannot be switched back even after poling the film using a high electric field and also heating the films above 220°C temperature. For both unstretched and stretched films, the peaks become sharper and more intense upon 60 Mrad irradiation in comparison to non-irradiated and 40 Mrad irradiated films. The increase in the coherence length of X-ray diffraction is due to the disappearance of the ferroelectric ordering and hence, ferroelectric domains. As the irradiation increases further, the shape of the X-ray peak becomes Lorentz type suggesting that the crystallite-amorphous interface is also quite diffused and crystallite size becomes very small.

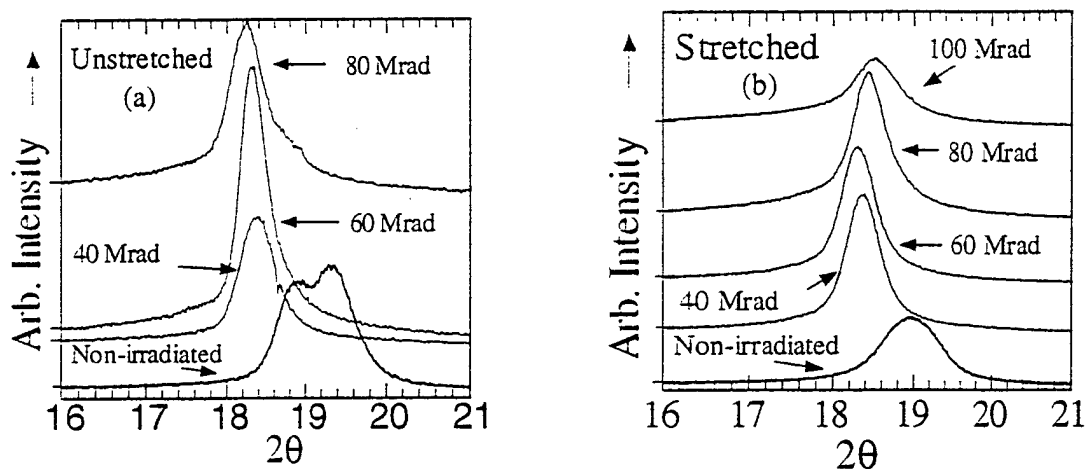


Figure 15: X-ray diffraction scans of (a) unstretched (b) stretched. P(VDF-TrFE) 50/50 mol % copolymer films irradiated with different doses at 95°C, using 2.55 MeV electrons.

3.b DSC Results:

The thermal properties of the copolymer also undergo a great change upon irradiation. Figures 16 (a) and (b) summarize the DSC results obtained from the unstretched and stretched 50/50 mol% copolymer films irradiated with different doses at 95°C, using 2.55 MeV electrons, respectively. Being ferroelectric in nature, the peak that appeared at 65°C is due to ferroelectric

to paraelectric (F-P) transition while the peak at 160 °C is due to the melting of crystallites. Consistent with X-ray results the crystal melting peak for stretched films is sharper and more intense than unstretched films and thus, reflects the higher crystalline ordering for stretched films. After the irradiation, the temperature and the enthalpy of the melting peak decreases continuously with increasing the irradiation dose for both unstretched and stretched films. The shift in temperature and broadening of the melting peak is higher for the unstretched films in comparison to the stretched films. The apparent shift and broadening of the melting peak indicates the presence of broad distribution in crystallite sizes and reduction in crystal ordering in irradiated films, which is due to the lattice defects and crosslinking within the crystallites or at crystallites-amorphous boundaries. Assuming that the enthalpy of the melting is directly proportional to the crystallinity in the sample, the change of crystallinity with dose can be deduced and is presented in figure 17(a). Clearly, the change of crystallinity with the dose acquired from the X-ray data, is consistent with that from the DSC data, although the DSC data yields a slightly lower crystallinity.

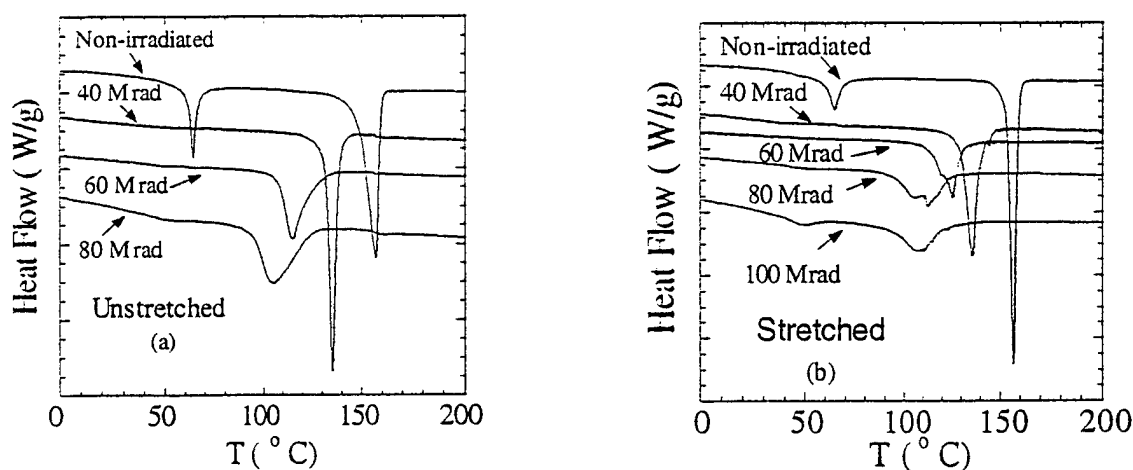


Figure 16 : DSC thermogram (a) unstretched, and (b) stretched. P(VDF-TrFE) 50/50 mol % copolymer non-irradiated, and irradiated with with 2.55 MeV electrons for different doses at 95°C.

Interestingly, a broad DSC peak reappears at temperatures near the original F-P transition peak position of non-irradiated films when the dose is increased to 80 Mrad and beyond. This is consistent with the X-ray data where at high doses the X-ray peak moves back to higher angle. The finding here indicates that the structural defects introduced by irradiation in the crystalline region depends on the crystallite size and also the boundary conditions at the crystalline-amorphous interface.

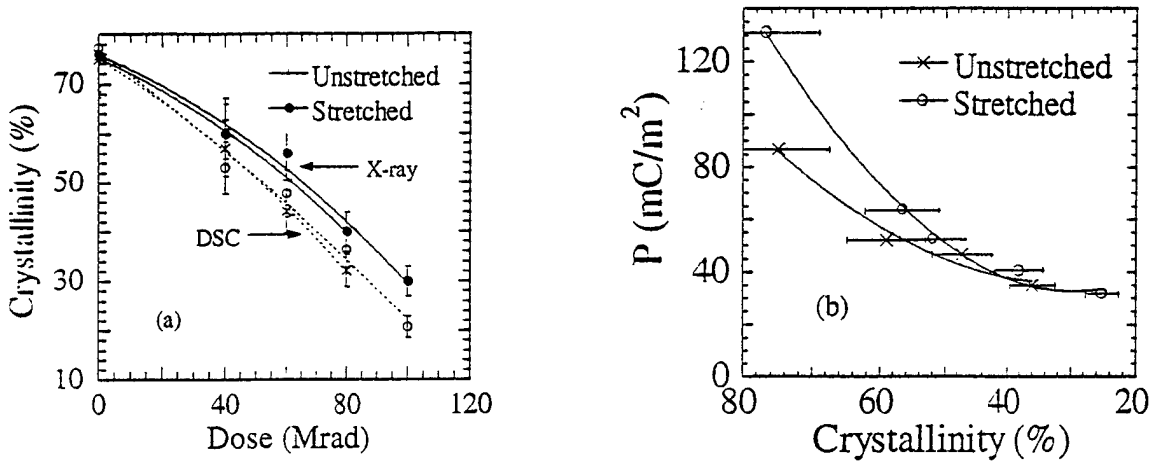


Figure 17 : Change (a) in the crystallinity with irradiation dose, calculated from X-ray data and DSC data and, (b) in induced polarization (P) at 160 MV/m field with the averaged value of the crystallinity obtained from figure A measured from P(VDF-TrFE) 50/50 mol % copolymer non-irradiated, and irradiated with 2.55 MeV electrons for different doses at 95°C.

It is well known that the morphology of P(VDF-TrFE) copolymers is that of crystallites embedded in an amorphous matrix, which is analogous to a composite structure. It is interesting to compare the results obtained here on the polarization and crystallinity (approximately the volume fraction of the crystallites in the polymer). Figure 17(b) presents the polarization P induced by 160 MV/m field as a function of crystallinity, which is taken from the averaged value of the DSC and X-ray data. Apparently, the initial drops of the crystallinity at low dose range (40 Mrad) causes a large reduction in the polarization for both stretched and unstretched

films. As has been pointed out, the initial precipitant decrease of the polarization in the stretched films is also partly caused by the reduction in the crystallite orientation in the irradiation process. Therefore, if the crystallinity of the polymer under 40 Mrad dose can be raised, due to the high ratio of the polarization/crystallinity for the copolymer studied here at this particular dose the polarization level can be improved markedly, especially in stretched films.

3.c FTIR Study:

Since IR is very sensitive to the molecular conformation, the FTIR measurements were carried out in order to further quantify the changes in the copolymer due to irradiation. The 50/50 mol% copolymer films, irradiated for different doses with 2.55 MeV electrons at 95°C were selected for this study. Although there are several peaks for each type of copolymer conformation, the peaks at 1288, 614 and 510 cm^{-1} which correspond to the presence of all trans ($T_{m \geq 4}$), TG and T_3G chains sequences, respectively, were selected to analyze the irradiation effect. The Lorentzian function was fitted to separate the component from each individual band. The samples used for investigation have slight variation in thickness and also the absorptivity for the same conformation might be different for each sample due to different crosslinking densities. In order to eliminate the effects due to these factors, the band at 3022 cm^{-1} , which is due to the C-H band vibration and is almost proportional to the thickness of the sample is selected as an internal standard. The change in the absorbance of each vibration with respect of internal standard was calculated. Furthermore, in order to quantify the changes due to irradiation, the change in molecular fraction (F_i) corresponding to $T_{m \geq 4}$, T_3G and TG chain sequences was calculated using the following expression :

$$F_i = \frac{A_i}{A_I + A_{II} + A_{III}} \quad (3)$$

where $I = I_I, I_{II}$ and I_{III} and A_I, A_{II} , and A_{III} are the absorbance of all trans ($T_{m \geq 4}$), T_3G and TG sequences, respectively. As can be observed in figure 18(a) after 40 Mrad irradiation molecular fraction of all trans sequences decreases drastically. While the molecular fraction for T_3G and TG chains sequences increases. These results support the fact that at first irradiation breaks all trans chains ($T_{m \geq 4}$) and generate T_3G and TG chains sequences by introducing the gauche bonds. Consistent with the polarization data the rate of decrease in fractional absorbance corresponding to all trans conformation is higher for stretched films than unstretched films.

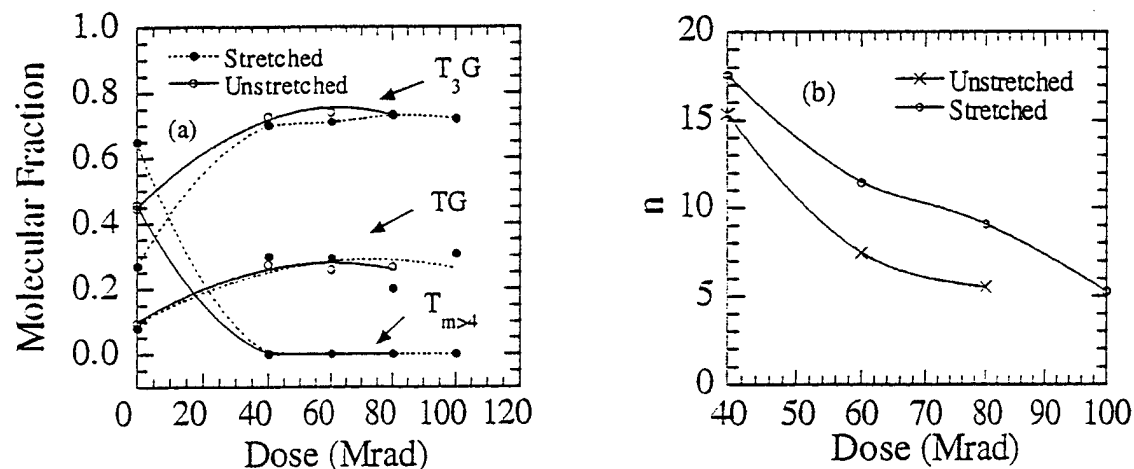


Figure 18 : Change in (a) molecular fraction corresponding to all trans ($T_{m \geq 4}$), T_3G and TG chain sequences and, (b) number of repeating units (n) between two crosslinks; for unstretched and stretched, P(VDF-TrFE) 50/50 mol % copolymer non-irradiated, and irradiated with different doses at 95°C using 2.55 MeV electrons.

In addition, after irradiation, a peak appeared at 1717 cm^{-1} , indicating the presence of the double bond structure of $\text{CH}=\text{CF}$ as well as carboxyl group ($-\text{C}=\text{O}$) and also a broad peak of hydroxyl ($-\text{OH}$) group between 3200 to 3600 cm^{-1} . It is believed that there is small chain scissioning as well as formation of carboxylic acid due to the presence of oxygen during the

irradiation. Even though irradiation was carried out under a continuous flow of nitrogen gas, a small amount of oxygen may still exist in the irradiation chamber.

3.d Crosslinking Results:

Crosslinking density was measured to provide information on the effect of crosslinking between the chains on the properties investigated here. Figure 18(b) presents the change in the number of repeating units (n) between two crosslink points along the chain in unit of $-\text{CH}_2-\text{CF}_2-\text{CHF}-\text{CF}_2-$, as a function of dose for both stretched and unstretched 50/50 mol% films irradiated with different doses at 95°C using 2.55 MeV electrons. The lower the value of n the greater the crosslinking density. Clearly, for stretched films at doses below 80 Mrad, the crosslinking increases with dose at a much lower rate compared with unstretched films. This indicates that the chain orientation introduced by stretching reduces the rate of crosslinking in the irradiation process. Also for stretched films at doses from 80 to 100 Mrads, the rate of the crosslinking with dose becomes much higher than that for unstretched films. As has been shown, irradiation has the effect of randomizing the orientation (crystallites and polymer chains) induced by stretching. At higher dosages the local chain orientation in stretched films may not be very much different than in unstretched films.

It was observed that for both unstretched and stretched films, the crosslinking increases in proportion to the decrease in the crystallinity. Furthermore, even with the same crystallinity the crosslinking of unstretched films is higher than that in stretched films. In other words, the reduction of the crystallinity in the copolymer under irradiation is not directly controlled by the crosslinking density, but it is expected that the crosslinking process has a significant role here in the conversion from the crystalline to amorphous phase in the copolymer.

The influence of crosslinking on the ferroelectric behavior and polar ordering in the crystalline region is not clear. From the data presented, it seems that as far as the field induced

polarization is concerned, the effect of crosslinking density is not significant and direct. However, the crosslinking density has a direct effect on the crystallite size, which may affect the polar response in the copolymer when the size of crystallites becomes small.

Publications:

I. Papers published in refereed journals:

1. Q. M. Zhang, Vivek Bharti, and X. Zhao, "Giant Electrostrictive Response and Ferroelectric Relaxor Behavior in Electron Irradiated Polyvinylidene Fluoride- Trifluoroethylene Polymer",
Science, 280, 2101-2104 (1998).
2. X. Zhao, Vivek Bharti, Q.M. Zhang, T. Ramotowski, F. Tito, and R. Ting, "Electromechanical Properties of Electrostrictive P(VDF-TrFE) Copolymer",
Appl. Phys. Lett., 73, 2054-2056 (1998).
3. Vivek Bharti, X. Zhao, Q.M. Zhang, T. Ramotowski, F. Tito, and R. Ting, "The Field Induced Strain and Polarization Response in Electron Irradiated Poly(vinylidene fluoride-trifluoroethylene) Copolymer",
J. Mater. Res. Innovations, 2(2), 57-63 (1998).
4. Z.-Y. Cheng, T.-B. Xu, Vivek Bharti, Shexi Wang, and Q.M. Zhang, "Transverse Strain Response in the Electrostrictive P(VDF-TrFE) Copolymer",
Appl. Phys. Lett. 74, 1901-1904 (1999).
5. Z.-Y. Cheng, Vivek Bharti, T. B. Xu, Shexi Wang, Q.M. Zhang, T. Ramotowski, F. Tito, and R. Ting., "Transverse Strain Responses in Electrostrictive P(VDF-TrFE) Films and Development of a Dilatometer for the Measurement",
J. Appl. Phys., 86, 2208-2214 (1999).

6. Vivek Bharti, Z-Y Cheng, S. Gross, T.B. Xu, and Q.M. Zhang, "High Electrostrictive Strain under High Mechanical Stress in High Energy Electron Irradiated Poly(vinylidene fluoride-trifluoroethylene) Copolymer Films",
Appl. Phys. Lett., 75, 2653-2655 (1999).
7. Vivek Bharti, H.S. Xu, G. Shanthi, Q.M. Zhang, and Kuming Liang, "Polarization and Structural Properties of High Energy Electron Irradiated P(VDF-TrFE) Copolymer Films",
J. Appl. Phys., 87, 452-461 (2000).
8. Vivek Bharti, G. Shanthi, H. Xu, Q. M. Zhang, and K. Liang, "Evolution of Transitional Behavior and Structure of Electron Irradiated P(VDF-TrFE) Copolymer Films",
Mater. Lett., accepted (2000).
9. Q. M. Zhang, Z. Y. Cheng, and Vivek Bharti, "Relaxor Ferroelectric Behavior in High Energy Electron Irradiated P(VDF-TrFE) copolymers",
Appl. Phys., A70, 307-312 (2000).
10. Z. Y. Cheng, V. Bharti, T. Mai, T. B. Xu, Q.M. Zhang, K. Hamilton, T. Ramotowski, K.A. Wright, and R. Ting, "Effect of High Energy Electron Irradiation on the Electromechanical Properties of Poly(vinylidene fluoride-trifluoroethylene) 50/50 and 65/35 Copolymers",
IEEE Trans. UFFC, accepted (2000).
11. Haisheng Xu, G. Shanthi, V. Bharti, Q.M. Zhang, and T. Ramatowski, "Structural, Conformational, and Polarization Changes of P(VDF-TrFE) Copolymer Induced by High Energy Electron Irradiation",
Macromolecules, accepted (2000).

12. Shizhuo Yin, Q. M. Zhang, K.-W. Chung, R. Yang, Z. Y. Cheng, and Yu Lu.,
 "Investigation of the Electro-optic Properties of Electron-irradiated P(VDF-TrFE)
 Copolymer",
Opt. Eng., 39, 670-672 (2000).
13. Vivek Bharti, Z.-Y. Cheng, T. Mai, Q.M. Zhang, T. Ramotowski, K.A. Wright, "High
 Electromechanical Coupling Factor and Electrostrictive Strain over a Broad Frequency
 Range in Electrostrictive Poly(vinylidene fluoride-trifluoroethylene) Copolymer",
 Submitted to *J. Appl. Phys.* (2000).

Papers published in proceedings:

1. Q. M. Zhang, Vivek, Bharti, Z-Y Cheng, and X. Zhao, "Relaxor Ferroelectric Polymers",
Proc. 1998 ISAF11, 439-442 (Montreux, Switzerland, 1998).
- 2 Z.-Y. Cheng, V. Bharti, X. Zhao, Shexi Wang, T. -B. Xu, and Q. M. Zhang, "Relaxor
 Ferroelectric Polymers for Actuators and Transducers",
Proc. 1998 IEEE Ultrasonic Symposium, 581-584 (Sendai, Japan, 1998).
3. Vivek Bharti, T. B. Xu. and Q. M. Zhang, "Correlation Between Large Electrostriction and
 Relaxor Behavior with Structural Changes Induced in P(VDF-TrFE) Copolymer by Electron
 Irradiation",
Proc. MRS Boston Meeting, Vol. 541, 653-659 (1998).
4. Q. M. Zhang, V. Bharti, Z.Y. Cheng, X. Z. Zhao, F. Tito, T. Ramotowski, and R. Ting,
 "Electromechanical Behavior of Electrostrictive P(VDF-TrFE) Copolymers",
Proc.1999 SPIE Conf. Smart Structures and Materials, Vol. 3669, 134-144 (Newport
 Beach, CA, 1999).

4. S. J. Gross, V. Bharti, Z-Y. Cheng, and Q. M. Zhang, "Mechanical Load Effects on the Electrostrictive Strain of P(VDF-TrFE) Copolymer",
Proc. 1999 IEEE Inter. Symp. Ultrasonics, 1019-1023 (Lake Tahoe, NE, 1999).
6. V. Bharti, Z. Y. Cheng, H. Xu, G. Shanthi, T. B. Xu, Q. M. Zhang, "Effect of Processing and High Energy Irradiation Conditions on the Electro-Mechanical and Structural Properties of P(VDF-TrFE) Copolymers",
Proc. MRS Boston Meeting, Vol. 600 (1999).
7. Z.Y. Cheng, S. Gross, V. Bharti, T. B. Xu, Q. M. Zhang, "Electromechanical Properties of Electron Irradiated P(VDF-TrFE) Copolymers",
Proc. MRS Boston Meeting, Vol. 600, (1999).
8. Q. M. Zhang, Z. Y. Cheng, V. Bharti, T. B. Xu, H. S. Xu, T. Mia, S. Gross, "Piezoelectric and Electrostrictive Polymer Based Actuator Materials"
Proc. of SPIE's 7th Ann. International Symp. on Smart Struct. and Mater., Vol. 3987 (Newport Beach, CA 2000).
9. Z. Y. Cheng, T. B. Xu, V. Bharti, and Q. M. Zhang, "Characterization of Electrostrictive P(VDF-TrFE) Copolymer Films for High-frequency and High-load Applications",
Proc. of SPIE's 7th Ann. International Symp. on Smart Struct. and Mater. Vol. 3987 (Newport Beach, CA 2000).
10. Q. M. Zhang, Z. Y. Cheng, V. Bharti, "Electrostrictive P(VDF-TrFE) Copolymers",
Proc. Materials Congress 2000 (Cirencester, UK).

11. R. Y. Ting and Q. M. Zhang, "New Electrostrictive PVDF Copolymers for Large-strain Actuator Application",
Proc. the EOS/SPIE Symposium on Applied Photonics, Vol. 4073 (Glasgow, UK, 2000).

III. Books:

Electroactive Polymers, Q. M. Zhang, T. Furukawa, Y. Bar-Cohen, and J. Scheinbeim.
Editors (Proceedings of Materials Research Society, Vol. 600, 1999).

IV. Patent:

Q.M. Zhang and Vivek Bharti. "*Relaxor Ferroelectric Polymers*" Filed (1998).